

DIRECT IODINATION OF BENZENE

COMPOUNDS.

by

Donald M. Hetler,  
A.B., University of Kansas, 1919,

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Approved by:

F. B. Davis  
Instructor in charge

H. P. Cade  
Chairman of Department

May, 1923.

This page is reserved for the expression of my thanks to Dr. F. B. Dains for his timely help and many suggestions, and to Dr. R. Q. Brewster for his assistance and suggestions.

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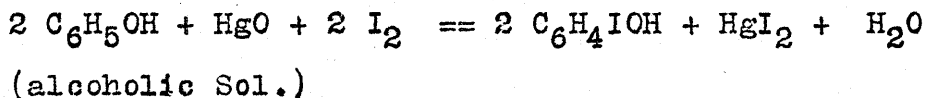
# DIRECT IODINATION OF BENZENE COMPOUNDS.

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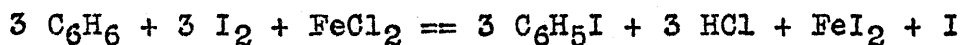
The object of this work is to continue the investigation started by H. A. Nelson<sup>1</sup> in 1917 who undertook his researches through the suggestion of the work of Messrs. Basik La Datta~~g~~ and Nihar Ranjan Chatterjee in the laboratories at Presidency College, Calcutta, India.<sup>2</sup>

The direct introduction of Iodine into organic compounds has been investigated at various times. Iodine in many respects reacts as does chlorine and bromine. Yet it does not enter into combination with organic compounds, particularly the Aromatic compounds directly. Basic compounds such as  $C_6H_5NH_2$  will substitute iodine directly. As a result an oxidizing agent must precede the introduction of Iodine by oxidizing away the hydrogen and then letting the iodine enter. Kekule<sup>3</sup> first used iodic acid. Hlasiwitz and Weselsky<sup>4</sup> used  $HgO$  in the following manner

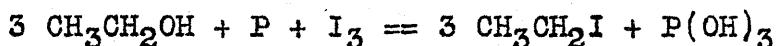
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1. H. A. Nelson, Thesis, (1917)
  2. J.A.C.S. 39, 435 (1917)
  3. C. 1870 63.
  4. Ann. 131-122; 174, 99



~~Lothar~~ meyer used Ferric chloride<sup>5</sup>



Hofmann<sup>6</sup> used yellow phosphorous and Beilsteen<sup>7</sup> the red



Lal Data<sup>8</sup> also mentions a modified method for the use of Phosphorous in the preparation of  $\text{C}_3\text{H}_5\text{I}$ . Potassium Persulphate and sulphur iodide were also used.

The first recorded instance of the use of nitric acid is by Deyer and Mixter<sup>9</sup> who dissolved oxanilid in acetic acid and then added iodine and nitric acid. In a short time a violent reaction took place and they obtained a forty per cent yield of iod-oxanilide. The next instance is that of Messrs. Chatterjee and Lal. Datta. They have by this method successfully prepared derivatives of benzene, toluene, xylene, cymene, mesitylene, hexane, throphene, ethyl benzene, naphthalene, and arthracene. They did not

5. Ann. 231-195

6. Ann. 126-250.

7. Ann. 115-273.

8. J.A.C.S. 36-1007.

9. Am. 8-352.

specify any other method than that of mixing the substance with iodine, heating to a desired temperature and adding nitric acid in small proportions until the reaction was complete.

Mr. Nelson<sup>1</sup> tried the method with success on brom-benzene, chlor-toluene, benzoic acid benzene, anisole and acetanilide. He obtained partial success on orth- and meta- chlor-toluenes and did not obtain positive results on di-brom-benzene, iod-benzene, nitro-benzene, para-chlor-toluene, anisidine, or phenacetin.

He assumed as did Lal Datta that the iodine enters directly as no HI was evolved and in all of his experiments an excess of the organic substance was used. Where good yields were obtained they were calculated from the iodine used as an initial charge.

Nitric acid also does not act as a catalytic agent as a copious quantity of nitric oxide fumes are evolved. Hence it enters into the reaction itself. Evidently the hydrogen of the ring is oxidized away and the iodine enters directly. The previous investigators found that the reaction was not applicable where the chances of nitration were greater than those of iodination. It is also evident in some cases that where the nitric acid content is too great hydrolysis

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1. H. A. Nelson, Thesis, (1917).

takes place with the formation of phenols as in the case of benzene.

The following experimental work was undertaken to see if some of the compounds which failed to produce a reaction at the temperature and acid concentration used by Nelson would not react under different conditions. The main method was that used by Nelson and Lal Datta with the exception that the temperature was greatly increased and the addition of the acid made more frequently and in larger amounts. The acid was added in from two to four cc. amounts and at intervals of time depending upon the speed of reaction but always when the evolution of the red fumes of nitric oxide had ceased to evolve in noticable quantities. The progress of the reaction could be easily followed by the diminution of the quantity of iodine which came up into the condenser and by the quantity of nitric oxide fumes evolved. When the reaction was complete the addition of further acid did not cause the evolution of red fumes.

The apparatus used was the same as that used by Mr. Nelson with the exception that the glass condenser tube was larger and the upper end enclosed in a water jacket. The reaction flask consisted of a two hundred fifty cc. kjeldahl flask. This was fitted

to a three foot glass tube by grinding the two together with turpentine and emery dust so as to form a ground glass joint. A cork or rubber joint would not last at the temperature used and with the nitric acid. The water jacket was fitted to the upper end of this tube leaving a space of about a foot and a quarter to act as an air condenser so as not to crack the tube by the sudden change of temperature which the water jacket would cause.

A long solid glass rod was used to dislodge all iodine which collected in the tube during the reaction. The temperature was maintained by means of a metal bath thus avoiding all fumes of an oil bath and also permitting the use of higher temperatures.

Some of the products formed have not been entirely identified because of the difficulty and length of time required to synthesize them by other means. Following is a tabulated summary of the compounds treated with the products they gave and a few of their physical properties.



Substance Treated	Products Formed	Temp. Used	Melting Point		
			Given	Obs.	
$\text{C}_6\text{H}_6$	$\text{C}_6\text{H}_5\text{I}$	140° 160°			
	Pictic acid	"	120°	122°	
$\text{C}_6\text{H}_5\text{I}$	P-- $\text{C}_6\text{H}_4\text{I}_2$	230°	127°	127°	
	O-- $\text{C}_6\text{H}_4\text{I}_2$	230°	40° - 50°	27°	
$\text{C}_6\text{H}_4\text{Br}_2$ (1,4)	P- $\text{C}_6\text{H}_3\text{Br}_2\text{I}$ (2)	390° 410°	45° - 48°	38°	
	P- $\text{Br}_2\text{C}_6\text{H}_4\text{I}_2$ (2-5)	"	136° - 139°	---	
$\text{C}_6\text{H}_5\text{NO}_2$	M- $\text{C}_6\text{H}_4(\text{NO}_2)_2$	270°			
$\text{C}_6\text{H}_4\text{-CH}_3\text{-Cl}$ 1 4	$\text{C}_6\text{H}_3(\text{CH}_3)\text{ClI}$ 1 3 4 3	215° 235°			
	$\text{C}_6\text{H}_4\text{COOH Cl}$ 1 4	"	236°	236°	
	$\text{C}_6\text{H}_2\text{CH}_3\text{Cl I}_2$ 1 4 (3,5?)	"		86°	
	? $\text{C}_6\text{H}_3\text{COOHClI}$ 1 4 3	"	210°?	220°	
$\text{C}_6\text{H}_4\text{COOHCl}$ 1 4	$\text{C}_6\text{H}_3\text{COOHClI}$ 1 4 3	290°	210°?	208°	
$\text{C}_6\text{H}_4\text{CH}_3\text{Cl}$ 1 2	$\text{C}_6\text{H}_3\text{CH}_3\text{ClI}$ 1 2 3?	205°			
	$\text{C}_6\text{H}_3\text{CH}_3\text{ClI}$ 1 2 5	"	--	18°	
	$\text{C}_6\text{H}_4\text{COOHCl}$ 1 2	"	137°	136°	
	$\text{C}_6\text{H}_3\text{COOHClI}$ 1 2 3	"	210°	195°	
	$\text{C}_6\text{H}_3\text{COOHClI}$ 1 2 5	"	148°?	143° 147°	
$\text{C}_6\text{H}_4\text{COOH Cl}$ 1 2	$\text{C}_6\text{H}_3\text{COOHClI}$ 1 2 5	250°	148°?	147°	
$\text{C}_6\text{H}_4\text{CH}_3\text{Cl}$ 1 3	$\text{C}_6\text{H}_3\text{CH}_3\text{ClI}$ 1 3 ?	220° 230°			

	Boiling Point		Yield	Pure	Iodine	Content
	given	obs.	grms.	%	Found	Calculated
	180° 187°	186°	25	77	62.20 62.15	62.25
			25	61.8	76.90 76.86	76.97
			2	33	34.78 34.88	35.09
			3	49	52.21 51.95	52.09
		135° 145°	10	50	50.40 50.33	50.29
					66.84 66.98	67.11
			6	55	44.02 44.26	44.95
	135° 140°	140°	55	69	50.04 49.93	50.29
	135° 140°					
			3	28	44.99 45.10	44.95
	200°	235° 245°	14	70	49.44 49.47	50.29
	50 MM					

## Benzene

A trial run was made on benzene in order to become familiar with the method.

25 cc of benzene and twenty grams of iodine were heated to  $140^{\circ}$  and the nitric acid added in three cc. portions. The reaction started quite vigorously and in a short time a noticeable decrease in the iodine content of the mixture had taken place. The temperature was now kept between  $140^{\circ}$ - $160^{\circ}$  for an hour and a quarter and nitric acid added as the brown red fumes became noticeably less copious until thirty five cc. of acid had been added. Practically all the iodine was used up.

The reaction product was worked free from acid, treated with  $\text{Na}_2\text{S}_2\text{O}_3$  to dissolve all free iodine and steam distilled. After distilling the product was dried with  $\text{CaCl}_2$  and distilled. That fraction boiling between  $180^{\circ}$ - $187^{\circ}$  was caught. The weight of pure product was 25 grams which was 77%.

A residue was left in the steam distillation flask which was solid and of a light yellow color. Upon crystallization it melted at  $120^{\circ}$  and was thought to be picric acid as Nelson and Lal Datta obtained this product.

## Iodine determination. (By Liquid ammonia)

Wt. of sample

I	II		I	II
21.8472	21.7063	AgNO <sub>3</sub>	16.00	15.00
<u>21.8063</u>	<u>21.5849</u>	NH <sub>4</sub> CNS	5.59	6.06
.1409	.1214			

$$1 \text{ cc NH}_4\text{CNS} = .986 \text{ cc AgNO}_3$$

$$1 \text{ cc AgNO}_3 = .008362 \text{ grs. I}_2$$

$$\text{I. } 5.59 \times .986 = 5.52 \quad 16.00 - 5.52 = .048 \text{ cc. AgNO}_3$$

$$\frac{10.48 \times .008362}{.1409} = 62.20\% \text{ I}_2$$

$$\text{II. } 6.06 \times .986 = 5.98 \quad 15.00 - 5.98 = 9.02 \text{ cc. AgNO}_3$$

$$\frac{9.02 \times .008362}{.1214} = 62.15 \% \text{ I}_2$$

$$\text{Calc. for C}_6\text{H}_5\text{I} = 62.25 \% \text{ I}_2$$

## Iod-Benzene.

Twenty-five grams of iod-benzene and twenty-five grams of iodine were heated to a temperature of  $230^{\circ}$ . Thirty cc. of nitric acid were added in three to four cc. portions until there was no more evolution of brown fumes. An hour was required for this reaction. The dark colored mass was washed with water and steam distilled from an alkaline solution. The distillate which was a mass of white crystals was dried on a porous plate and partially recrystallized from alcohol. During this recrystallization the alcohol evaporated unnoticed and the di-iod-benzene was sublimed around the edge of the dish. On this account the entire mass was sublimed. It was obtained in thin leaflike crystals. The melting point was  $127^{\circ}$  which is the same as Richter gives for para-di-iod-benzene. Twenty-five grams of pure product were obtained giving 61.8 % calculated from the iod-benzene.

## Iodine determination by liquid ammonia

I	II		I	II
.1327	.1108	$\text{AgNO}_3$	15.00	15.00
		$\text{NH}_4\text{CNS}$	286	499

$$1 \text{ cc. } \text{NH}_4\text{CNS} = .986 \text{ cc. } \text{AgNO}_3$$

$$1 \text{ cc. } \text{AgNO}_3 = .008362 \text{ grs. } \text{I}_2$$

$$\text{I. } 2.86 \times .986 = 2.80; \quad 15.00 - 2.80 = 12.20;$$

$$\frac{12.20 \times .008362}{1327} = 76.90 \% \text{ I}_2$$

$$\text{II. } 4.99 \times .986 = 4.82; \quad 15.00 - 4.82 = 10.18;$$

$$\frac{10.18 \times .008362}{.1108} = 76.86 \% \text{ I}_2$$

$$\text{Calc. for } \text{C}_6\text{H}_4\text{I}_2 = 76.97 \% \text{ I}_2$$

A small liquid residue was left in the flask after steam distillation. Upon cooling it solidified. After repeated recrystallizations a solid was obtained which gave an impure melting points, which ranged from 40°-50°. Ortho-di-iod-benzene melts at 27°. Evidently the product which was a very small amount was a mixture of ortho- and para- di-iod-benzene.

Nitro-Benzene

Eight grams of nitro-benzene and eight and a half grams of iodine were heated to a temperature of 270°. Nitric acid was added in small amounts until twenty-five cc. had been added. The time required was one hour and forty five minutes. At the end of this time, the iodine had appreciably disappeared from the condenser and it was thought that the reaction was nearly completed. Upon examination of the product almost all of the iodine was found in a ball in the bottom of the flask. The oil was separated from the nitric acid and iodine and steam distilled from an alkaline solution. The distillate gave no test for iodine nor was there any product left in the flask after distillation.

A second trial was made with the same quantities of iodine and nitro-benzene. The temperature was raised to 320° to 350° and maintained there for two hours and a half. Altogether forty cc. of acid were used. During the entire reaction it was very difficult to keep the iodine in the reaction flask. For the last half hour it volatilized from the solution of acid and nitro-benzene as fast as it was shoved back into it. The oil was separated from the acid, worked with water and steam distilled

from an alkaline solution. The distillate gave no test for iodine and when distilled after drying with  $\text{CaCl}_2$  it came over between  $208^\circ$ - $220^\circ$  pure nitro-benzene boils at  $210^\circ$ .

A very small amount of a yellow amorphous compound was formed in the acid after standing over night. When filtered from the acid and worked it dissolved in the water giving it a yellow tinge. The amount was so small that not enough could be obtained to give a good melting point. It is probably meta-di-nitro-benzene.

(P) Di-Brom-Benzene

Twelve grams of Para-di-brom-benzene was mixed with seven grams of iodine and heated to two hundred fifty degrees. Upon the addition of nitric acid in three cc. portions a slight reaction occurred. The temperature was raised to three hundred and more nitric acid added. The reaction did not proceed any faster after a half hour period. The temperature was raised to three hundred fifty and still a slight reaction. When a temperature between three hundred ninety and four hundred ten was used the reaction progressed a little faster. After two hours at this temperature the reaction was stopped as no further progress was noted. The reason for this was thought to be due to the great excess of nitric acid in the chamber as sixty cc. were used. Considerable excess Iodine was left in the condenser. The product in the reaction flask was a white solid mixed with some Iodine. This was washed with water and then dilute alkali.

The product was then steam distilled from an alkaline solution. Unchanged (p) di-brom-benzene came over at first quite rapidly. Upon further steam distillation a semi-solid oil came over followed by a white crystalline solid.



The oil was dissolved in ninety per cent alcohol and the first products coming out of solution were filtered off. After several such crystallizations the oil could not be further purified. It finally crystallized in white crystals which melted between  $45^{\circ}$ - $48^{\circ}$ . Iodine determinations showed it to be mono-iod-di-brom-benzene which Richter gives as melting at  $38^{\circ}$  C.

The other solid was likewise crystallized from ninety per cent alcohol and gave a melting point between  $136^{\circ}$ - $139^{\circ}$ . Iodine determinations showed it to be a di-iod- (P) Di-Brom-Benzene. The Iodine probably occupying the 2,5 positions.

A second trial was made using four grams of Di-Brom-Benzene and four grams of Iodine, with an initial temperature of three hundred ninety. Nitric acid was added in 3 cc. portions and a violent reaction took place immediately. After using twenty cc. of acid and maintaining a temperature between  $390^{\circ}$  and  $410^{\circ}$  for one hour and a quarter all the Iodine had disappeared. The crystalline product was separated from the acid washed with warm water and steam distilled. No unchanged (P) di-brom-benzene came over. The first distillate was a semi-solid oil. The second portion was a mass of white crystals.

The first portion was now fractionally crystallized from ninety-per cent alcohol. After several such crystallizations a solid was obtained which melted between 45°-59° which was the same as obtained from the first trial. Iodine determinations were as follows:

Sample		Titration	
I	II	I	II
.1214	.1105	AgNO <sub>3</sub> 25.94	16.64
		NH <sub>4</sub> CNS 10.95	2.85

$$1 \text{ cc. N H}_4\text{CNS} = .986 \text{ cc. AgNO}_3$$

$$1 \text{ cc. AgNO}_3 = .008362 \text{ grs. I}_2$$

$$\text{I. } 10.95 \times .986 = 10.79 \text{ cc.}; \quad 25.94 - 10.79 = 15.15 \text{ cc.}; \quad 15.15 \div 3 = 5.05 \text{ cc.}$$

$$\frac{5.05 \times .008362}{.1214} = 34.78 \% \text{ I}_2$$

$$\text{II. } 2.85 \times .986 = 2.81 \text{ cc.}; \quad 16.64 - 2.81 = 13.83 \text{ cc.}; \quad 13.83 \div 3 = 4.61 \text{ cc.}$$

$$\frac{4.61 \times .008362}{.1105} = 34.88 \% \text{ I}_2$$

$$\text{Calc. for C}_6\text{H}_3\text{Br}_2\text{I} = 35.09$$

It is evident that this compound is (2) Iod (1,4) di-Brom-benzene which melts at 38° according to Richter.

Two grams of this product were obtained giving a percentage calculated from the Di-Brom-Benzene as 33 %.

The second solid was crystallized from ninety per cent alcohol and gave a melting point of 137°-141° iodine content shows that it is (2,?) Di-Iod (1,4) Di-Brom-Benzene.

The iodine determinations are as follows:

Sample		Titration	
I	II	I	II
.0843	.0783	cc AgNO <sub>3</sub>	15.59
		cc NH <sub>4</sub> CNS	16.06
			5.14
			6.58

$$1 \text{ cc. NH}_4\text{CNS} = .986 \text{ cc. AgNO}_3$$

$$1 \text{ cc. AgNO}_3 = .008362 \text{ grs. I}_2$$

$$\text{I. } 5.14 \times .986 = 5.07; \quad 15.59 - 5.07 = 10.52;$$

$$10.52 \div 2 = 5.26$$

$$\frac{5.26 \times .008362}{.0843} = 52.21 \% \text{I}_2$$

$$\text{II. } 6.58 \times .986 = 6.34; \quad 16.06 - 6.34 = 9.72;$$

$$9.72 \div 2 = 4.86$$

$$\frac{4.86 \times .008362}{.0783} = 51.95 \% \text{I}_2$$

$$\text{Calculated for C}_6\text{H}_2\text{Br}_2\text{I}_2 = 52.09 \% \text{I}_2$$

This is probably the (2,5) di-iod, (1,4) di-brom-benzene. Richter does not give any of the di-iod-di-brom benzene with an established melting point.

Three grams of this product were obtained which corresponds to a yield of 49 %.

(P) Chlor-Toluene

Ten grams of (P) chlor-toluene were heated with seven grams of Iodine to a temperature ranging between 215°-235°, mostly at 220°. Thirty five cc. of acid were added in three cc. amounts until the most of the iodine had disappeared. The total time was two hours and forty minutes. The product consisted of an oil, dark colored with iodine. This oil was separated from the acid washed with water and decolorized with dilute sodium hydroxide.

The oil was steam distilled, leaving a white solid in the flask. This solid was crystallized from alcohol and gave a melting point of 85°.

The yield was very small. Iodine determinations gave the following results:

Sample		Titration	
I.	II	I	II
.1276	.1483	AgNO <sub>3</sub> 20.00	20.00
		NH <sub>4</sub> CNS 4.77	2.21

$$1 \text{ cc. NH}_4\text{CNS} = .986 \text{ cc. AgNO}_3$$

$$1 \text{ cc. AgNO}_3 = .008362 \text{ gr. I}_2$$

$$I. \quad 4.77 \times .986 = 4.70; \quad 20.00 - 4.70 = 15.30;$$

$$15.30 \times \frac{2}{3} = 10.20;$$

$$\frac{10.20 \times .008362}{.1276} = 66.84 \% \text{ I}_2$$

$$\text{II. } 2.21 \times .986 = 2.18; \quad 20.00 - 2.18 = 17.82;$$

$$17.82 \times 2/3 = 11.88;$$

$$\frac{11.88 \times .008362}{.1483} = 66.98 \% \text{ I}_2$$

$$\text{Calculated for } \text{C}_7\text{H}_5\text{ClI}_2 = 67.11 \% \text{ I}_2$$

This is evidently a di-iod (P) chlor-toluene probably the 3,5 di-iod. As the mono product was the (3) iod (p) chlor toluene as will be shown.

The distillate from the steam distillation was dried with calcium chloride and distilled under a vacuum of 11 mm. A few cc. came over up to 135° C. the main fraction then practically distilled between 135° and 145°, Mostly at 140°. The remainder just a couple of cc. decomposed after reaching that temperature, liberating much iodine.

Iodine determinations were made on this fraction, which indicated it was practically a pure mono-iod (P) chlor-toluene. The yield was ten grams or a percentage of 50 % calculated from the para-chlor-toluene.

Iodine determinations were as follows:

Sample		Titration		
I	II		I	II
21.7541	21.5803	AgNO <sub>3</sub>	25.00	20.00
<u>21.5803</u>	<u>21.4468</u>	NH <sub>4</sub> CNS	4.12	3.98
.1738	.1335			

$$1 \text{ cc. } \text{NH}_4\text{CNS} = .986 \text{ cc } \text{AgNO}_3$$

$$1 \text{ cc. } \text{AgNO}_3 = .008362 \text{ grs. } \text{I}_2$$

$$\text{I. } 4.12 \times .986 = 4.06; \quad 25.00 - 4.06 = 20.94;$$

$$20.94 \div 2 = 10.47$$

$$\frac{10.47 \times .008362}{1738} = 50.40 \% \text{ I}_2$$

$$\text{II. } 3.98 \times .986 = 3.93; \quad 20.00 - 3.93 = 16.07;$$

$$16.07 \div 2 = 8.035$$

$$\frac{8.035 \times .008362}{.1335} = 50.33 \% \text{ I}_2$$

$$\text{Calc. for } \text{C}_7\text{H}_5\text{ClI} = 50.29 \% \text{ I}_2$$

The proof of the position of the iodine in this compound will be taken up under the head of para-chlor-benzoic acid.

The sodium hydroxide extraction was neutralized with hydrochloric acid and as a result an organic acid was precipitated. This acid was thoroughly washed with cold water and a fractional separation was performed by heating in small amounts of hot water and collecting the precipitated acid which separated on cooling. In this manner the acid was divided into two parts one of which gave no qualitative test for iodine and which melted at  $236^\circ \text{C}$ . Richter gives the melting points of para-chlor-benzoic acid at  $236^\circ$ . Evidently that is what this acid was.

The second acid was repeatedly recrystallized from water and also from dilute alcohol and the best melting point that could be obtained was between  $218^{\circ}$  and  $224^{\circ}$ . A qualitative test for iodine was made and the presence of iodine was shown. A molar weight determination gave the following results:

Sample	Titration	
	Acid	Base
1,000 gr.	12.95	20.00

$$1 \text{ cc B.} = .928 \text{ cc A.}$$

$$20.00 \times .928 = 18.56 \text{ cc. Acid; } 18.56 - 12.95 = 5.61 \text{ cc acid.}$$

$$\text{N. of acid} = .1033 = .005066 \text{ gr. H}_2\text{SO}_4$$

$$5.61 \times .005066 = .02842 \text{ gr. H}_2\text{SO}_4$$

$$.02842: 49.04 :: .1000:x$$

$$.02842 x = 4.904$$

$$x = 172 = \text{M. W. of acid.}$$

This shows the acid to be a mixture of para-chlor benzoic acid and iod (p) chlor-benzoic acid. Para-chlor benzoic has a molar weight of 156.5. Iod-para-chlor-benzoic has a molar weight of 282.5 This would show the acid to contain about eight per-cent of the iod-para-chlor-benzoic acid.



Para-Chlor-Benzoic Acid

Para-Chlor-benzoic Acid was prepared from para-chlor toluene by the method of Ulman.<sup>10</sup> The melting point was determined as 235°C.

Six grams of the acid and 5 grams of iodine were heated to 250°C. and nitric acid added in 3 cc. portions. There was no evident reaction and the temperature was raised to 270° and more nitric acid added. There was no reaction at this temperature so it was raised to 290°-300° and a violent reaction started in less than twenty minutes at this temperature the reaction was complete. All together thirty five cc. of acid were used and the total time was one hour and fifteen minutes.

The product which was obtained contained no free iodine and was insoluble in acid. It was purified by crystallizing from dilute alcohol and gave a melting point of 210°-212°. Sublimation was now tried on the product and fine white crystals were obtained which melted at 208°C.

The total yield of purified products was six grams or 55 % calculated from the parachlor-benzoic acid.

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10. Am. Ch. J. 16, 533.

Iodine determination gave the following:

Sample		Titration		
I	II		I	II
.1442	.1517	AgNO <sub>3</sub>	20.00	20.00
		NH <sub>4</sub> CNS	4.90	4.00
		1 cc. NH <sub>4</sub> CNS = .986 cc. AgNO <sub>3</sub>		
		1 cc. AgNO <sub>3</sub> = .008362 gr. I <sub>2</sub>		

I.  $4.90 \times .986 = 4.83$ ;  $20.00 - 4.83 = 15.17$ ;  
 $15.17 \div 2 = 7.59$

$$\frac{7.59 \times .008362}{.1442} = 44.02 \% I_2$$

II.  $4.00 \times .986 = 3.94$ ;  $20.00 - 3.94 = 16.06$ ;  
 $16.06 \div 2 = 8.03$

$$\frac{8.03 \times .008362}{.1517} = 44.26 \% I_2$$

$$\text{Calc. for } C_7H_4O_2ClI = 44.95$$

A sample of the Iod-(p) chlor toluene was oxidized by the method of Ulman<sup>10</sup> although the time of heating was much prolonged. This product was washed several times with cold water and crystallized from dilute alcohol. A melting point determination gave 206°C. A mixed melting point with this acid and the one mentioned above melted at 207°C. evidently they are the same acid.

Iodine determination gave the following:

Sample		Titration	
I	II	I	II
.0828	.0908	AgNO <sub>3</sub> 15.12	15.03
		NH <sub>4</sub> CNS 6.29	5.35
		1 cc. NH <sub>4</sub> CNS = .986 cc. AgNO <sub>3</sub>	
		1 cc. AgNO <sub>3</sub> = .008362 gr. I <sub>2</sub>	

$$\text{I. } 6.29 \times .986 = 6.20; \quad 15.12 - 6.20 = 8.92;$$

$$8.92 \div 2 = 4.46$$

$$\frac{4.46 \times .008362}{.0828} = 45.04 \% \text{ I}_2$$

$$\text{II. } 5.36 \times .986 = 5.29; \quad 15.03 - 5.29 = 9.74;$$

$$9.74 \div 2 = 4.87$$

$$\frac{4.87 \times .008362}{.0908} = 44.90 \% \text{ I}_2$$

$$\text{Calc. for } \text{C}_7\text{H}_4\text{O}_2\text{ClI} = 44.95 \%$$

To prove the constitution of these acids, and as one of the acids was the oxidation product of the iod (P) chlor toluene, the following procedure was followed. Five grams of the para-chlor-benzoic acid were mixed with ten grams of pulverized potassium nitrate. This mixture was slowly added to fifteen cc. of 100 % sulphuric acid, shaking thoroughly through the addition. The solution was now kept at a tem-

perature of  $70^{\circ}$  -  $80^{\circ}$  for one half hour by means of a water bath. Upon cooling the solution solidified into a solid mass. This mass was added to cold water and the excess sulphuric acid, nitric acid and potassium salts washed out. The resulting nitro-para-chlor benzoic acid was dried and gave a melting point of  $175^{\circ}$ - $176^{\circ}$ . According to Richter this is 3 nitro 4, chlor, benzoic acid which melts at  $178^{\circ}$ - $180^{\circ}$ . Five grams of product were obtained.

This (3) nitro, (4) chlor, benzoic acid was now reduced by the method of Hunn<sup>11</sup>. The resulting product was the (3) amino, (4) chlor benzoic acid which melted at  $214^{\circ}$  (Richter gives  $216^{\circ}$ - $217^{\circ}$ ).

Iodine was now added to the compound in place of the amine group by means of the Sandmeyer reaction. The product was crystallized several times from dilute alcohol and gave a melting point of  $210^{\circ}\text{C}$ .

Iodine determinations gave the following result:

Sample		Titration	
I	II	I	II
15.00	1 6.45	$\text{AgNO}_3$ 20.00	20.00
		$\text{NH}_4\text{CNS}$ 4.10	2.58
		1 cc. $\text{NH}_4\text{CNS}$ = .986 cc. $\text{AgNO}_3$	
		1 cc. $\text{AgNO}_3$ = .008362 grs. $\text{I}_2$	

$$\text{I. } 4.10 \times .986 = 4.04; \quad 20.00 - 4.04 = 15.96;$$

$$15.96 \div 2 = 7.98$$

$$\frac{7.98 \times .008362}{.1500} = 44.49 \% \text{ I}_2$$

$$\text{II. } 2.58 \times .986 = 2.54; \quad 20.00 - 2.54 = 17.46;$$

$$17.46 \div 2 = 8.73$$

$$\frac{8.73 \times .008362}{.1645} = 44.38 \% \text{ I}_2$$

$$\text{Calc. for } \text{C}_7\text{H}_4\text{O}_2\text{ICl} = 44.95 \% \text{ I}_2$$

Mixed melting points were now run with this acid and the other two.

With the acid obtained through the iodation reaction the result was 210°-211). With the acid obtained by oxidizing some of the iod-para-chlor-toluene the result was 207°-208°.

These mixed melting points thus prove the three acids to be identical and thus establish the position of the iodine as that of number three. Hence the product obtained by iodating the para-chlor-toluene is (4)Cl, (3)I, toluene, and the product obtained by iodating the (p) chlor-benzoic acid is the (3)I, (4)Cl benzoic acid.

Ortho-chlor-toluene

Forty grams of O. chlor-toluene were added to thirty grams of iodine and heated to 205°C. Nitric acid was added in three cc. portions at intervals, depending upon the amount of brown fumes coming off. Altogether forty cc. of acid were used. The total time was two and a half hours.

The product consisting of a dark colored oil was separated from the acid and washed in ten per cent alkali. The alkali removed the oxidized products and excess iodine. Upon the addition of hydrochloric acid the organic acid separated out. The total weight was one gram. Upon heating with water a product was obtained which gave no qualitative test for iodine and which melted at 136°C. This is ortho-chlor-benzoic acid which Richter gives as melting at 137°. The remaining acid gave qualitative tests for iodine. Fractional crystallization gave two products one of which melted at 143°-147° and corresponds to the (5) Iod. (2) chlor.benzoic acid which will be described later. The other melted around 195° and evidently must be impure (3) Iod (2) chlor benzoic acid which Richter gives as melting at 210°. There was not sufficient of these acids to run iodine determinations.

The liquid obtained by the reaction was now steam distilled from an alkaline solution. It distilled very slowly except the first few cc. which had the odor of orthochlor-toluene and were discarded. The distillate was dried with calcium chloride and distilled under reduced pressure varying between 11 and 21 mm. The main portion came over between 135° and 140° and was a light yellow oil. Fifty five grams of this product were obtained which corresponds to a 69 % yield calculated from the (O) chlor-toluene.

Iodine determinations gave the following:

Sample		Titration	
I	II	I	II
21.7633	21.6470	AgNO <sub>3</sub>	20.16 43.40
21.7460	21.3554	NH <sub>4</sub> CNS	6.33 8.70
<u>.1163</u>	<u>.2916</u>	1 cc. NH <sub>4</sub> CNS = .986 cc. AgNO <sub>3</sub>	
		1 cc. AgNO <sub>3</sub> = .008362 grs. I <sub>2</sub>	

$$\text{I. } 6.33 \times .986 = 6.24; \quad 20.16 - 6.24 = 13.92$$

$$13.92 \div 2 = 6.96$$

$$\frac{6.96 \times .008362}{.1163} = 50.04 \% \text{ I}_2$$

$$\text{II. } 8.70 \times .986 = 8.58; \quad 43.40 - 8.58 = 34.82;$$

$$34.82 \div 2 = 17.41$$

$$\frac{17.41 \times .008362}{.2916} = 49.93 \% \text{ I}_2$$

$$\text{Calc. for C}_7\text{H}_6\text{ICl} = 50.29$$

In order to obtain further information in regard to the constitution of this product, 5 cc. were nitrated with 15 cc. of fuming nitric acid at 0°. Two products were obtained, one a liquid, the other a solid. The solid was crystallized from ether and gave a melting point of 84°. This compound corresponds to the nitro-compound obtained by Mr. Long<sup>12</sup> which is the nitro product of (5) Iod (2) chlor toluene. A mixed melting point of the two compounds melted at 84°.

Iodine determination gave the following:

Sample		Titration	
I	II	I	II
.1673	.1847	AgNO <sub>3</sub>	20.00 20.00
		NH <sub>4</sub> CNS	3.02 1.14
		1 cc. NH <sub>4</sub> CNS = .986 cc. AgNO <sub>3</sub>	
		1 cc. AgNO <sub>3</sub> = .008362 grs. I <sub>2</sub>	

$$I. \quad 3.02 \times .986 = 2.98; \quad 20.00 - 2.98 = 17.02;$$

$$17.02 \div 2 = 8.51$$

$$\frac{8.51 \times .008362}{.1673} = 42.52 \% I_2$$

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$$\text{II. } 1.14 \times .986 = 1.12; \quad 20.00 - 1.12 = 18.88;$$

$$18.88 \div 2 = 9.44$$

$$\frac{9.44 \times .008362}{.1847} = 42.73 \% \text{ I}_2$$

$$\text{Calc. for } \text{C}_7\text{H}_5\text{O}_2\text{NClI} = 42.69$$

Kjeldahl determinations for nitrogen gave the following:

Sample			Titration		Blank
I	II		Sample I	II	
.1999	.2021	H <sub>2</sub> SO <sub>4</sub>	25.00	25.00	25.00
		NaOH	17.82	17.60	24.00
		N or H <sub>2</sub> SO <sub>4</sub> = 0.1033			
		1 cc NaOH = .940 cc. Acid.			

$$\text{Blank} \div 24.00 \times 94 = 22.56; \quad 25.00 - 22.56 = 2.44 \text{ cc. A.}$$

$$\text{I. } 17.82 \times .940 = 16.74; \quad 25.00 - 16.74 = 8.26;$$

$$8.26 - 2.44 = 5.82$$

$$\frac{5.82 \times .1033 \times .014}{.1999} = 4.31 \% \text{ N}_2$$

$$\text{II. } 17.60 \times .940 = 16.54; \quad 25.00 - 16.54 = 8.46;$$

$$8.46 - 2.44 = 6.02$$

$$\frac{6.02 \times 0.1033 \times .014}{.2021} = 4.31 \% \text{ N}_2$$

$$\text{Calc. for } \text{C}_7\text{H}_5\text{O}_2\text{NClI} = 4.70 \% \text{ N}_2$$

Iodine determinations on the Liquid nitro-product were as follows:

Sample		Titration		
I	II		I	II
21.3335	21.2329	AgNO <sub>3</sub>	15.50	15.00
<u>21.2329</u>	<u>21.1151</u>	NH <sub>4</sub> CNS	5.20	2.00
.1006	.1278			

$$1 \text{ cc. NH}_4\text{CNS} = .986 \text{ cc. AgNO}_3$$

$$1 \text{ cc. AgNO}_3 = .008362 \text{ grs. I}_2$$

$$I. \quad 5.20 \times .986 = 5.13; \quad 15.50 - 5.13 = 10.37;$$

$$10.37 \div 2 = 5.18$$

$$\frac{5.18 \times .008362}{1.006} = 43.06$$

$$\text{Calc. for C}_7\text{H}_5\text{O}_2\text{NClI} = 42.69 \% \text{ I}_2$$

Kjeldahl determinations for nitrogen gave the following results:

Sample		Titrations		Blank
I	II	Sample I	II	
23.0268	22.8438	H <sub>2</sub> SO <sub>4</sub>	25.00	25.00
		NaOH	17.82	16.83
		Nor. of H <sub>2</sub> SO <sub>4</sub> = 0.1033		
		1 cc. NaOH = 0.940 cc. acid		

$$\text{Blank P } 24.00 \times .940 = 22.56; \quad 25.00 - 22.56 = 2.44 \text{ cc.}$$

$$\text{I. } 17.82 \times .940 = 16.75; \quad 25.00 - 16.75 = 8.25;$$

$$8.25 - 2.44 = 5.81 \text{ cc.}$$

$$\frac{5.81 \times .0033 \times .014}{.1830} = 4.58 \% \text{ N}_2$$

$$\text{II. } 16.83 \times .940 = 15.72; \quad 25.00 - 15.72 = 9.28;$$

$$9.28 - 2.44 = 6.84$$

$$\frac{6.84 \times 0.1033 \times .014}{.2162} = 4.59\% \text{ N}_2$$

$$\text{Calc. for } \text{C}_7\text{H}_5\text{O}_2\text{NClI} = 4.70 \%$$

It seems that the Iod (0) Chlor-toluene from which this nitro product was derived is the (3) Iod (2) chlor. toluene.

Ortho-Chlor-Benzonic Acid

Ortho-chlor-toluene was oxidized by the method of Ulman<sup>14</sup> to ortho-chlor-benzoic acid.

Six grams of this acid and six grams of iodine were heated to 250°C. Upon the addition of nitric acid a reaction started. Nitric acid was added from time to time in three cc. portions until 25 cc. had been added. After one and a half hours practically all the iodine has disappeared. The nitric acid was drained from the solid mass in the bottom which was thoroughly washed with cold water. This product was repeatedly crystallized from boiling water. The final product weighing three grams was a slight yellowish crystal which gave no qualitative test for nitrogen and gave the following percentage of Iodine.

Sample		Titration	
I	II	I	II
0.1131	.1247	AgNO <sub>3</sub>	15.00      15.00
		NH <sub>4</sub> CNS	2.88      1.57
		1 cc. NH <sub>4</sub> CNS	= .986 cc. AgNO <sub>3</sub>
		1 cc. AgNO <sub>3</sub>	= .008362 grs. I <sub>2</sub>

$$\text{I. } 2.88 \times .986 = 2.84; \quad 15.00 - 2.84 = 12.16;$$

$$12.16 \div 2 = 6.08$$

$$\frac{6.08 \times .008362}{.1131} = 44.99 \% \text{ I}_2$$

$$\text{II. } 1.57 \times .986 = 1.55; \quad 15.00 - 1.55 = 13.45;$$

$$13.45 \div 2 = 6.725$$

$$\frac{6.725 \times .008362}{.1247} = 45.10 \% \text{ I}_2$$

$$\text{Calc. for } \text{C}_7\text{H}_4\text{O}_2\text{ClI} = 44.95 \% \text{ I}_2$$

This product melts between  $147^\circ$ - $149^\circ$ .

It is not the (3) iod, (2) chlor, benzoic acid as this acid melts at  $210^\circ$  (Richter). Therefore it was assumed to be the (5) iod. (2) chlor. benzoic acid. As this acid was unknown it was synthesized by the following method.

Five grams of (0) chlor benzoic and ten grams of pulverized potassium nitrate were thoroughly mixed, dissolved in fifteen cc. of 100 % sulphuric acid and kept at a temperature between  $70^\circ$ - $80^\circ$  for one half hour. The product was then poured into cold water, washed free from acid, dried and the melting point determined. This M. p. was  $160^\circ$ - $163^\circ$  which corresponds to the (5) nitro (2) chlor benzoic acid which Richter gives as melting at  $165^\circ$ .

This nitro acid was then reduced by the method of Hunn<sup>15</sup> and a small yield of a product which melted at 178°-182° was obtained. This corresponds to the m.p. of (5) amino (2) chlor benzoic acid which Richter gives as melting at 188°.

Iodine was introduced in place of the amino group by means of Sandmeyers reaction. A very small yield was obtained which was purified by crystallization from boiling water. This product gave a melting point of 138°-140°. A mixed melting between this iodo acid and the iodo acid prepared by the iodination method gave 141°-143°.

There was not sufficient of this synthesized acid to run an iodine determination.

From the mixed melting point it is evident that the Iodo acid obtained from treating ortho chlor benzoic acid is the (5) Iodo (2) chlor benzoic acid.

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Meta-chlor-toluene

Ten grams of Meta-chlor-toluene and ten grams of iodine were heated to a temperature of 220°-230°. Nitric acid was added in 3-4 cc. portions at varying intervals until thirty cc. had been added. After forty five minutes all of the iodine had disappeared. The acid was separated from the dark oil and the latter washed with dilute sodium hydroxide solution. A light colored oil was obtained. This oil was dried over solid sodium hydroxide and fractionally distilled under 50 mm. pressure. The first drop came over at 165°. The first fraction was cut at 185°, the second at 200°. The remaining oil now started to decompose so the distillation was stopped.

Iodine determinations on the first fraction showed a percentage of iodine of about 48 which is a little low as meta-chlor-iod-toluene has a percentage of 50.29.

Iodine determinations on the second portion are as follows:

Sample			Titration	
I	II		I	II
36.7538	36.5873	AgNO <sub>3</sub>	23.00 cc.	27.00 cc.
<u>36.5873</u>	<u>36.3773</u>	NH <sub>4</sub> CNS	3.35	2.20
.1665	.2096			

$$1 \text{ cc. } \text{NH}_4\text{CNS} = .986 \text{ cc. } \text{AgNO}_3$$

$$1 \text{ cc. } \text{AgNO}_3 = .008362 \text{ grs. } \text{I}_2$$

$$\text{I. } 3.35 \times .986 = 3.30; \quad 23.00 - 3.30 = 19.70$$

$$19.70 \div 2 = 9.85$$

$$\frac{9.85 \times .008362}{.1665} = 49.47 \% \text{ I}_2$$

$$\text{II. } 2.20 \times .986 = 2.16; \quad 27.00 - 2.16 = 24.84;$$

$$24.84 \div 2 = 12.42$$

$$\frac{12.42 \times .008362}{.2096} = 49.44 \% \text{ I}_2$$

This is still some what below the calculated percentage for iodine in iod-meta chlor-toluene which is 50.29 %.

The high boiling fraction was dark colored with liberated iodine. As a consequence it was treated with dilute sodium hydroxide, to remove this iodine, and dried over solid sodium hydroxide, Iodine determination gave the following:

Sample		Titration	
I	II	I	II
36.6976	36.5011	$\text{AgNO}_3$	25.00    35.00
<u>36.5011</u>	<u>36.2425</u>	$\text{NH}_4\text{CNS}$	2.23    5.17
.1965	.2586	1 cc. $\text{NH}_4\text{CNS} = .986 \text{ cc. } \text{AgNO}_3$	
		1 cc. $\text{AgNO}_3 = .008362 \text{ grs. } \text{I}_2$	



$$\text{I. } 2.23 \times .986 = 2.20; \quad 25.00 - 2.20 = 22.80;$$

$$22.80 \div 2 = 11.40$$

$$\frac{11.40 \times .008362}{.1965} = 48.50 \% \text{ I}_2$$

$$\text{II. } 5.17 \times .986 = 5.10; \quad 35.00 - 5.10 = 29.90;$$

$$29.90 \div 2 = 14.95$$

$$\frac{14.95 \times .008362}{.2586} = 48.35 \% \text{ I}_2$$

$$\text{Calc. for } \text{C}_7\text{H}_6\text{ClI} = 50.29 \%$$

The reason for the low percentage of iodine is partially due to the decomposition.

These two fractions correspond to the iod-meta-chlor-toluene as found by Nelson and described by Richter. Both of whom give the boiling point between 235°-245°. There was not sufficient time to determine the exact constitution of this compound. This must be left to further research.

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